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FEATURES OF THE ELECTRONIC STRUCTURE OF RUTHENIUM TETRACARBOXYLATES WITH AXIALLY COORDINATED NITRIC OXIDE (II)

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The electronic structure of $Ru_2(\mu\text{-}O_2CR)_4$, $Ru_2(\mu\text{-}O_2CR)_4(L)_2$ and $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ (R = H, CH_3, CF_3; L = H_2O, THF) ruthenium tetracarboxylates is analyzed on the basis of calculations by the density functional method with full geometry optimization. It is concluded that the axial coordination of nitric oxide (II) to $Ru_2(\mu\text{-}O_2CR)_4$ is accompanied by destruction of the metal-metal π-bond with d_π-AO Ru reorientation on bonding with NO molecules.

Keywords: density functional theory, tetracarboxylates, ruthenium, nitric oxide (II).

INTRODUCTION

The metal–metal bond order in binuclear tetracarboxylates of transition elements $M_2(\mu\text{-}O_2CH)_4(L)_2$ is characterized mainly by the nature of the metal and its oxidation level. The quadruple M–M bond is assigned to the tetracarboxylates with the (d^4–d^4) core and $(\sigma)^2(\pi)^4(\delta)^2$ (M = Mo, W) electron configuration [1]; but if metal ion has more than four *d*-electrons, then the molecular orbitals in the complex are partially filled being antibonding with respect to the metal-metal bond. Hence, the bond order reduces in comparison with a maximal value of 4. Rh(II, II) complexes with $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^2$ electron configuration are related to compounds with a single bond between metal atoms [1-3], whereas Ru_2(II, II) complexes with partially filled π* and δ* orbitals are related to compounds with a double bond [4, 5].

In the works of Norman et al. based on X_α scattered wave calculations [6, 7] the ground state of Ru_2(II, II) complexes was determined as a triplet with $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^3(\delta^*)^1$ configuration and it was noted that energies of π*- and δ*-orbitals were close to each other [7]. By ZINDO/S-MRCI calculations [8] of $Ru_2(\mu\text{-}O_2CH)_4$, the quintet ground state with $(\pi^*)^2(\delta^*)^1(\sigma^*)^1$ configuration was found and the triplet state with $(\pi^*)^2(\delta^*)^2$ configuration was obtained for $Ru_2(\mu\text{-}O_2CH)_4(L)_2$ (L = H_2O, pyrazine) complexes; in the same work the $(\pi^*)^2(\delta^*)^2$ triplet ground state was found for all Ru_2(II, II) compounds in question by DFT. In the recent publication [9], the electron coupling between metal centers in $M_2(\mu\text{-}O_2CH)_4$ tetracarboxylates (M = Mo, Tc, Ru, Rh) was analyzed based on Kohn–Shem diagrams obtained by DFT (PW91 functional) with full geometry optimization; the main state of $Ru_2(\mu\text{-}O_2CH)_4$ was determined as $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^2(\sigma^*)^0$ triplet.

It was determined in the experimental studies that in $Ru_2(\mu\text{-}O_2CR)_4(L)_2$ complexes the Ru–Ru, Ru–O_{bridge}, Ru–L bond lengths only slightly differ from the corresponding values for Ru_2(III, II) compounds and are weakly sensitive to the

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nature of L ligand in the R group [4]. The notable exceptions from the series of ruthenium tetracarboxylates are $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ diamagnetic compounds in which the Ru–Ru bond length is more than 2.5 Å [10], which is substantially more than in any other complexes from this series. These structural deviations are observed also in rhodium nitroso tetracarboxylates [11] and the work [12] is devoted to their study using DFT. An increase in the distance between metal atoms in the $M_2(X)_4$ core at the axial coordination of NO is also observed in ruthenium complexes with N-donor bridge ligands, where X are 2-fluoranilinpyridinate (Fap) and diphenylformamidinate (dpf) anions [13, 14]; in the work [14] the metal–metal bond lengthens from 2.444 Å in $Ru_2(dpf)_4(NO)$ to 2.632 Å in $Ru_2(dpf)_4(NO)_2$, with the corresponding decrease of the bond order from 1.5 to 1.0.

According to the metal–metal bond scheme suggested by Norman et al., the $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^2$ or $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^4$ electron configuration with six electrons on antibonding molecular orbitals was ascribed to $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ complexes. This helps us to explain the diamagnetism of these compounds and the increase in the Ru–Ru distance up to the values corresponding to a single bond [10]. However, the authors of the work [10] noted that due to close energies of *d*-AO Ru and NO π*-orbitals the bond picture must not be so simple. According to the *ab initio* calculations made to interpret photoelectron spectra [15]* the ground states of $Ru_2(\mu\text{-}O_2CH)_4$ and $Ru_2(\mu\text{-}O_2CH)_4(NO)_2$ complexes are the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^2$ triplet and $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^4$ singlet, respectively. In the review [4], ruthenium nitroso tetracarboxylates are considered as complexes with the $Ru_2(I, I)$ core and NO^+ axial ligands but the author of this review does not exclude the possibility of describing them as systems with a strong antiferromagnetic interaction between $Ru_2(II, II)$ and NO• radicals.

The aim of this work is to analyze the correlation between the geometrical and electronic structure of ruthenium(II) tetracarboxylates and reveal the specific character of nitric oxide(II) as an axially coordinated ligand using quantum chemical calculations with full geometry optimization.

As a calculation object the following compounds were chosen: $Ru_2(\mu\text{-}O_2CR)_4$, (R = H, CH_3, CF_3); $Ru_2(\mu\text{-}O_2CH)_4(H_2O)_2$, $Ru_2(\mu\text{-}O_2CH)_4(THF)_2$ (THF = tetrahydrofuran); $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ (R = H, CH_3, CF_3).

CALCULATION DETAILS

The calculations were performed using the density functional theory (DFT) with the hybrid functional B3LYP [16]. Two basis sets were used: 1) a valence LanL2DZ basis set [17, 18] with the effective core potential of ruthenium atom and 2) a combined basis set — 6-31G** for H, C, N, and O atoms and valence SDD with a corresponding pseudopotential for Ru [19]. In all cases, the geometry of complexes was optimized without imposing restrictions on symmetry, and the stationary points were identified based on the vibration spectrum calculations.

For all compounds, except $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$, B3LYP calculations presented in this work yield the triplet ground states with the $(\pi^*)^2(\delta^*)^2$ electron configuration (δ-orbitals oriented between bridge O atoms are filled; δ-orbitals directed to O bridge atoms are vacant). The calculations of $Ru_2(\mu\text{-}O_2CR)_4$ and $Ru_2(\mu\text{-}O_2CR)_4(H_2O)$ complexes performed by the CASSCF method (12 electrons on ten orbitals) in the LanL2DZ basis set produces the same result. It is worth noting that in $Ru_2(\mu\text{-}O_2CR)_4$ the optimized by CASSCF method (10 electrons on seven orbitals) Ru–Ru bond length is 2.416 Å and this is in worse agreement with experiment than that calculated by the B3LYP method in the same basis set. In the case of $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$, the singlet ground state is obtained by the B3LYP method. The results presented in tables and figures are obtained by the spin restricted (for $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$) and spin unrestricted (for all the other complexes) B3LYP methods.

Atomic charges and orbital populations were examined in the context of: 1) the Mulliken population analysis and 2) the analysis of natural atomic orbitals (NAO) [20]. In the description of chemical bonds together with the overlap

*The geometry optimization was not performed.

populations

$$Q(A-B) = 2\sum_{\mu\in A}\sum_{\nu\in B} P_{\mu\nu}\cdot S_{\mu\nu}$$

the bond order indices are suggested as a connecting link between quantum chemistry and the classical theory of the molecular structure [21, 22]:

$$B(A-B) = \sum_{\mu\in A}\sum_{\nu\in B}\left[(PS)_{\mu\nu}(PS)_{\nu\mu} + (P^tS)_{\mu\nu}(P^tS)_{\nu\mu}\right].$$

P^{α} and P^{β} are density matrices for the α and β spin projection; $P = P^{\alpha} + P^{\beta}$ is the full density matrix; $P^{t} = P^{\alpha} - P^{\beta}$ is the spin density matrix; S is the overlap matrix. For singlet states this expression reduces to

$$B(A-B) = \sum_{\mu\in A}\sum_{\nu\in B}(PS)_{\mu\nu}(PS)_{\nu\mu}.$$

In the case of orthogonal basis sets, the Mayer bond order is identical to the Wiberg index [23]

$$W(A-B) = \sum_{\mu\in A}\sum_{\nu\in B}\left|P_{\mu\nu}\right|^2,$$

which is considered as a bond index in the NAO basis set. The examination of the orbital nature of bonds is based on the analysis of natural orbitals of bonds (NBO) [20]. The geometry structure optimization and the NBO analysis were performed using GAUSSIAN-03 software complex [24]. The Mayer bond orders were calculated by PC GAMESS program [25,26]; PC GAMESS and GAUSSIAN-03 programs were used for the multiconfiguration calculations. To visualize the NBO Molekel 4.3 program was used [27]; molecular orbital diagrams were drawn and analyzed using the specially created MOBuilder program.

RESULTS AND DISCUSSION

Optimized in both basis sets the values of bond lengths (Tables 1-3) correctly reproduce the observed correlation between the structural characteristics of complexes with different composition; in comparison with the experimental data for the solid phase calculated for isolated complexes the *r*(Ru–Ru) distances are overestimated (especially in LanL2DZ basis set) (Table 1). Ru–O_{bridge} bond lengths are almost equal in all the compounds under consideration: 2.10-2.12 Å in LanL2DZ basis set and 2.07-2.11 Å in SDD/6-31G**. The Ru–Ru distance slightly depends of the substituents; after coordination of H_2O or THF molecules to $Ru_2(\mu\text{-}O_2CR)_4$ the metal–metal bond lengthens by not more than 0.05 Å, while the axial coordination of nitric oxide molecules results in the increase of the *r*(Ru–Ru) calculated values by 0.3 Å (Table 1).

Both the calculated and experimental [10] data illustrate a small deviation of Ru–N group from the straight line connecting two metal atoms: according to the calculations, ∠Ru–Ru–N is in a range of 162-165°. The RuNO group is bent in the same direction; the optimized values of the Ru–N–O angle in $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ complexes

Basis set	R=H	R=CH_3	R=CF_3
LanL2DZ	149.84	150.68	152.83
SDD/6-31G**	150.54	148.80	151.79

agree with experimental: 152.45° (R = Et) and 152.83° (R = CF_3) [10, 28].

Calculated in LanL2DZ basis set frequencies of stretching metal-metal vibrations for $Ru_2(\mu\text{-}O_2CR)_4$, $Ru_2(\mu\text{-}O_2CR)_4(H_2O)_2$, $Ru_2(\mu\text{-}O_2CR)_4(THF)_2$ complexes are in a region of 340 cm^{-1}, while those calculated in SDD/6-31G** basis set are in a region of 360 cm^{-1}, which is consistent with the suggested in the literature assignment of these vibrations to a region of ~350 cm^{-1} [4, 8, 29]. The ν(Ru–Ru) values for nitroso tetracarboxylates are shifted by 130-140 cm^{-1} to the low-frequency region and noticeably mixed with the bending vibrations of the $Ru_2(\mu\text{-}O_2CR)_4$ core (Table 1). The ν(N–O) experimental values are equal to 1756 cm^{-1} for $Ru_2(\mu\text{-}O_2CCH_3)_4(NO)_2$ and 1800 cm^{-1} for $Ru_2(\mu\text{-}O_2CCF_3)_4(NO)_2$ [10].

TABLE 1. Characteristics of Ru–Ru Bonds in $Ru_2(\mu\text{-}O_2CH)_4(L)_2$ from the Results of B3LYP Calculations

Basis	Parameter	Without ligand			H_2O	THF			NO		
		H	CH_3	CF_3	H	H	CH_3	CF_3	H	CH_3	CF_3
Experiment, [10, 28]	*r*(Ru–Ru)						2.261	2.277		2.515*	2.532
LanL2DZ	*r*(Ru–Ru)	2.309	2.298	2.323	2.340	2.349	2.336	2.371	2.613	2.593	2.613
	ν(Ru–Ru)	343	370	340	333	336	357	337	211	(204)	(173)
										214	221
	W(Ru–Ru)	1.26	1.24	1.25	1.16	1.14	1.14	1.096	0.52	0.50	0.51
	B(Ru–Ru)	1.87	1.86	1.88	1.78	1.81	1.81	1.758	0.66	0.63	0.65
SDD/6-31G**	*r*(Ru–Ru)	2.271	2.264	2.276	2.294				2.575	2.558	2.577
	ν(Ru–Ru)	364	384	369	362				220	212	229
									(256)	222	(263)
	W(Ru–Ru)	1.30	1.29	1.30	1.20				0.53	0.53	0.53
	B(Ru–Ru)	1.91	1.89	1.87	1.83				0.59	0.58	0.56

*Data for R=Et.

TABLE 2. Characteristics of Ru–L Bonds in $Ru_2(\mu\text{-}O_2CH)_4(L)_2$ from the Results of B3LYP Calculations

Basis	Parameter	H_2O	THF			NO		
		H	H	CH_3	CF_3	H	CH_3	CF_3
Exper. [10,28]	*r*(Ru–L)			2.390	2.268		1.781	1.790
LanL2DZ	*r*(Ru–L)	2.500	2.321	2.342	2.258	1.839	1.836	1.850
	W(Ru–L)	0.10	0.10	0.094	0.121	1.11	1.13	1.07
	B(Ru–L)	0.24	0.18	0.177	0.211	1.02	1.04	0.96
SDD/6-31G**	*r*(Ru–L)	2.401				1.821	1.818	1.829
	W(Ru–L)	0.10				1.14	1.16	1.11
	B(Ru–L)	0.32				1.01	1.03	0.96

TABLE 3. Calculated Characteristics of the N–O Bond in NO Molecule, NO^+ and NO^- ions, and in $Ru_2(\mu\text{-}O_2CH)_4(NO)_2$ Complex According to B3LYP Calculations

Parameter	Free ligand						$Ru_2(O_2CR)_4(NO)_2$					
	LanL2DZ basis set			SDD/6-31G** basis set			LanL2DZ basis set			SDD/6-31G** basis set		
	NO^+	NO	NO^-	NO^+	NO	NO^-	R=H	$R=CH_3$	$R=CF_3$	R=H	$R=CH_3$	$R=CF_3$
q(NO)Mul	+1	0	–1	+1	0	–1	–0.04	–0.06	0.03	–0.03	–0.06	0.01
$q(NO)_{NAO}$	+1	0	–1	+1	0	–1	0.07	0.05	0.15	0.07	0.04	0.13
R	1.106	1.199	1.333	1.073	1.159	1.279	1.194	1.198	1.184	1.159	1.162	1.154
ν(N–O)*	2219	1770	1290	2480	1991	1467	1729; 1749	1711; 1730	1776; 1795	1883; 1906	1864; 1887	1911; 1934
W(N–O)	2.80	2.09	1.39	2.79	2.10	1.40	1.92	1.90	1.99	1.92	1.90	1.96
B(N–O)	2.64	2.11	1.63	2.63	2.16	1.69	1.69	1.67	1.76	1.67	1.65	1.70
Q(N–O)	0.79	0.41	0.16	0.96	0.56	0.25	0.54	0.53	0.56	0.58	0.56	0.59

*Two values of frequencies that correspond to asymmetrical and symmetrical (forbidden) vibrations are given for the complexes.

According to spin-unrestricted B3LYP calculations performed in this work, the $(\sigma_\alpha)^1(\sigma_\beta)^1(\pi_\alpha)^2(\delta_\alpha)^1(\pi_\beta)^2(\delta_\beta)^1(\pi^*_\alpha)^2(\delta^*_\alpha)^1(\delta^*_\beta)^1$ configuration corresponds to the ground state of $Ru_2(\mu\text{-}O_2CR)_4$. This configuration describes the distribution of twelve electrons on the upper occupied spin-orbitals localized mainly on the {Ru–Ru} fragment. The energy of the $(\sigma_\alpha)^1(\sigma_\beta)^1(\pi_\alpha)^2(\delta_\alpha)^1(\pi_\beta)^2(\delta_\beta)^1(\pi^*_\alpha)^2(\delta^*_\alpha)^1(\delta^*_\alpha)^1$ quintet state for $Ru_2(\mu\text{-}O_2CH)_4$ is by 0.56 eV higher (according to B3LYP/LanL2DZ calculations with geometry optimization). The transition from LanL2DZ basis set to SDD/6-31G** does not change the order of orbitals but results in the increase in their energies. The change of the energies of higher occupied orbitals when the R substituent varies is determined by its inductive effect: in the substitution of R = H for R = CF_3 the energy decreases because of the electron density drawn off from the Ru–Ru bond area to CF_3, and in the substitution for R = CH_3 it increases. The calculated energy values (eV) of the upper occupied δ^*_β spin-orbitals (or, in the case of L=NO, δ*-orbitals) are listed below:

Basis set	Without ligand			L=H_2O	L=THF			L=NO		
	H	CH_3	CF_3	H	H	CH_3	CF_3	H	CH_3	CF_3
LanL2DZ	–5.98	–5.36	–7.76	–5.18	–4.81	–4.35	–6.40	–6.72	–6.23	–8.11
SDD/6-31G**	–5.52	–4.96	–6.54	–4.89	—	—	—	–6.25	–5.81	–7.05

At the axial coordination of σ-donor H_2O and THF ligands there is still one electron* on π^*_x and π^*_y spin-orbitals; twelve upper occupied spin-orbitals stay localized on metal atoms and their energies are increasing as compared with $Ru_2(\mu\text{-}O_2CR)_4$. Thus, the electron configuration of the metal core in $Ru_2(\mu\text{-}O_2CH)_4(H_2O)_2$ and $Ru_2(\mu\text{-}O_2CH)_4(THF)_2$ is $(\pi_\alpha)^2(\sigma_\alpha)^1(\sigma_\beta)^1(\delta_\alpha)^1(\delta_\beta)^1(\pi_\beta)^2(\pi^*_\alpha)^2(\delta^*_\alpha)^1(\delta^*_\beta)^1$, and the formal configuration of each ruthenium atom is $(\sigma)^1(\pi)^3(\delta)^2$.

Nitric oxide coordination is accompanied by noticeable changes of the complex electron structure. Due to the mixing of ruthenium d_π-orbitals with NO π*-orbitals, the contribution of Ru *d*-AO to π*-orbitals of the metal core decreases and their full occupation becomes energetically favorable (Figs. 1, 2, Table 4). Hence, the ground state has the closed electron shell with $(\pi)^4(\delta)^2(\pi^*)^4(\sigma)^2(\delta^*)^2$ configuration describing the distribution of fourteen electrons on the upper occupied molecular orbitals mainly localized on the {ON–Ru–Ru–NO} fragment. This configuration differs from that suggested in the work [10] only by the position of d_{z^2}(Ru1) + d_{z^2}(Ru2) σ-orbital. It should be noted that total populations of σ, π, and δ *d*-AO of each ruthenium atom in $Ru_2(\mu\text{-}O_2CH)_4(NO)_2$ stays almost the same as in other $Ru_2(\mu\text{-}O_2CH)_4(L)_2$ tetracarboxylate complexes.

Without ligand			L=H_2O			L=THF			L=NO		
σ	π	δ	σ	π	δ	σ	π	δ	σ	π	δ
1.08	3.03	2.74	1.11	3.05	2.56	1.14	3.05	2.56	1.18	3.06	2.60

The increased population of δ-orbitals in comparison with a formal value of 2 for $(\sigma)^1(\pi)^3(\delta)^2$ configuration is explained by the participation of vacant $d_{x^2-y^2}$ -AO of Ru in the σ-bond with orbitals of a bridge and O→Ru charge transfer. The order of the upper occupied orbitals and the energy gaps between them in $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ complexes are almost equal in LanL2DZ and SDD/6-31G** basis sets and hardly change depending on R.

The results given above indicate a considerable difference in the geometric and electron structure characteristics of $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ from similar characteristics of other ruthenium tetracarboxylates. The electronic structure features of nitroso complexes are most pronounced in the examination of metal–metal bond indices (Table 1) and in the analysis of natural orbitals of the bonds. The Mayer and Wiberg bond indices *B*(Ru–Ru) and *W*(Ru–Ru), listed in Table 1, indicate a small weakening of the bond between metal atoms during the coordination of water and tetrahydrofuran molecules. In the case of nitric oxide, these values doubly decrease; therefore we can discuss the change in the metal-metal bond order.

*Hereafter it is supposed that the metal–metal bond line coincides with the *z* axis.

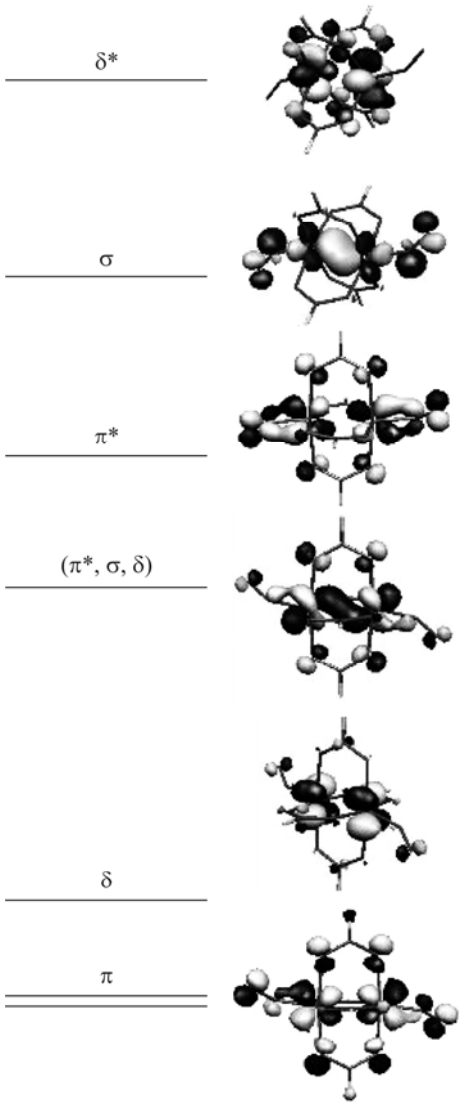

Fig. 1. Upper occupied orbitals of the $Ru_2(\mu\text{-}O_2CH)_4(NO)_2$ complex.

TABLE 4. Energies (ε, eV) of the Upper Occupied Orbitals of $Ru_2(\mu\text{-}O_2CH)_4(L)_2$ Complexes and the Contribution of Metal (*m*, %) and Ligand L (*l*, %) AO According to B3LYP/LanL2DZ* Calculations. For the Complexes with Open Shells the Results for the Spin-Orbitals with α and β Spins are Given

Orbital	Without ligand				L=H_2O						L=THF						L=NO		
	α		β		α			β			α			β					
	ε	*m*	ε	*m*	ε	*m*	*l*	ε	*m*	*l*	ε	*m*	*l*	ε	*m*	*l*	ε	*m*	*l*
π*	–6.38	85			–5.86	88	2				–5.36	83	8				–7.54	49	27
π*	–6.94	85			–5.92	88	2				–5.56	89	0				–7.66	65	11
δ*	–6.94	85	–5.97	75	–5.56	74	0	–5.14	78	0	–5.19	75	0	–4.77	78	0	–6.70	69	1
δ	–7.87	85	–7.45	85	–6.97	86	0	–6.55	86	0	–6.56	77	12	–6.15	86	0	–8.05	75	8
π	–8.67	32	–7.51	76	–7.71	49	4	–6.37	81	2	–7.67	26	34	–5.78	75	12	–8.24	39	22
π	–8.67	32	–7.51	76	–7.79	50	1	–6.38	82	1	–7.39	51	0	–5.98	84	0	–8.26	40	20
σ	–9.54	89	–9.24	92	–7.32	73	18	–7.13	80	14	–6.60	71	6	–6.37	67	30	–7.33	56	41

*Calculations by GAMESS program.

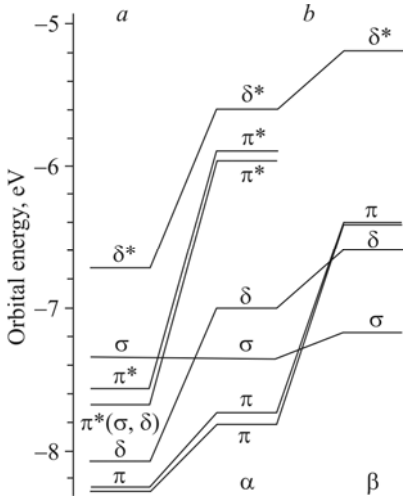

Fig. 2. Diagrams of the upper occupied orbitals of $Ru_2(\mu\text{-}O_2CH)_4(NO)_2$ (*a*) and $Ru_2(\mu\text{-}O_2CH)_4(H_2O)_2$ (*b*) complexes.

The natural bond orbital allows us to understand the above differences. For each $Ru_2(\mu\text{-}O_2CR)_4$ and $Ru_2(\mu\text{-}O_2CR)_4(L)_2$ (R = H, CH_3, CF_3; L = H_2O, THF) compound four bonding singly populated NBO are obtained. These orbitals describe the double bond between the metal centers: σ_α and σ_β generated by d_{z^2}-orbitals of Ru atoms, and two π-NBO (with the equal spin projection) generated by d_{xz} and d_{yz} orbitals. In the $Ru_2(\mu\text{-}O_2CR)_4$ complex, the σ*(Ru–Ru) NBO has low population. The donor-acceptor bond of Ru atoms with axial ligands L is realized mainly owing to the electron density transfer from the oxygen atom lone pair of the L ligand to this NBO and the increase in its population results in a small decrease of the metal-metal bond order and in the increase in the length (Table 1).

In the case of complexes with L=NO, the bond picture considerably changes (Table 1, Fig. 3):

— the NBO of the π-type bonding the metal atoms are absent;

— the population of σ NBO(Ru–Ru) decreases and the population of σ* NBO(Ru–Ru) increases, which results in a noticeable weakening of the σ-bond between the metal atoms;

— four bonding and four antibonding NBO with Ru d_π (d_{xz} and d_{yz}) AO are found; these orbitals describe the bond of each metal atom with NO ligand coordinated to it.

The electrons on bonding NBO are responsible for the covalent component of the bond between atoms; the electrons on antibonding NBO contribute to noncovalent interactions [20]. The population of Ru–N bonding NBO exceeds 1.6, of antibonding is close to 0.4*. The results obtained indicate the substantially covalent character of Ru–NO π-bonds. In their generation one lone π-electron from each of the two axially coordinated NO molecules “embeds” into the group of electrons on the upper occupied complex orbitals.

The characteristics of the N–O bond in $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ and in free NO, NO^+, and NO^- complexes are compared in Table 3. For NO^+, NO, and NO^- the experimental value of r(N–O) is equal to 1.063 Å, 1.151 Å, and 1.260 Å respectively; ν(N–O) are 2377 cm^{-1}, 1904 cm^{-1} [30] (or 1875 cm^{-1} [31]) and 1470 cm^{-1} [30, 31]. The absolute values of charges on the coordinated NO molecule (Table 3) do not exceed 0.1 unit of the electron charge. The internuclear distance r(N–O), the frequency of stretching vibrations ν(N–O), the Wiberg index W(N–O), and the overlapping population Q(N–O) for $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ are close to the corresponding values for a free uncharged NO molecule; the Mayer bond order values are slightly different from the corresponding values for NO^-. None of the characteristics under consideration conforms with the

*On average for the calculations in two basis sets.

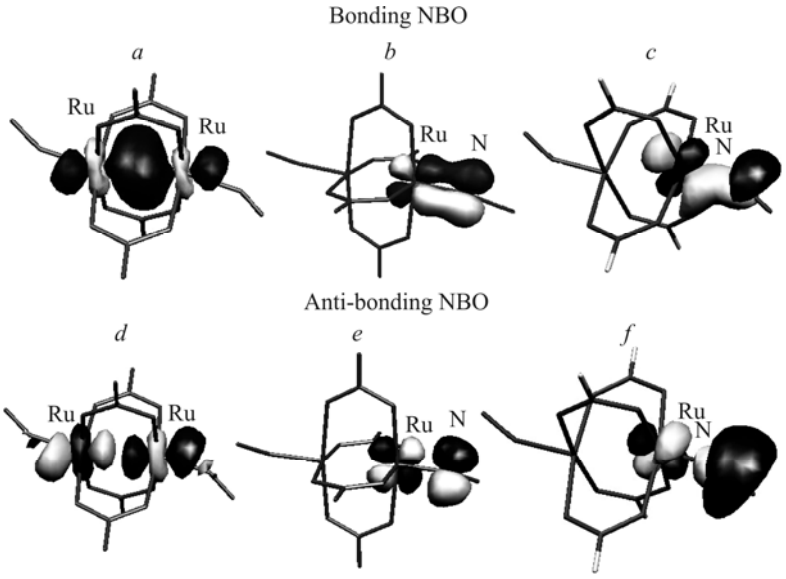

Fig. 3. Natural bond orbitals (NBO) responsible for metal-metal bonds (*a, d*) and one of metal atoms with neighboring N atom (*b, c, e, f*) in the $Ru_2(\mu\text{-}O_2CH)_4(NO)_2$ complex.

interpretation of $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ complexes as combinations of Ru(I, I) and NO^+.

All the above stated allows us to speak about a strong "intervention" of coordinated NO molecule orbitals in the electron structure of the Ru–Ru metal core that is accompanied by the destruction of metal-metal π-bonds and the reorientation of ruthenium d_π-orbitals to the formation of Ru–NO covalent bonds. The unique ability of nitric oxide to π-bonding with ions of transition metals is well known. If metal *d*-orbitals and NO π*-orbitals are close in energies, they are strongly mixed, and it is impossible to unambiguously relate the electron pair of the formed bond to metal ion or NO. In 1966 Jorgensen [32] called the ligands, whose presence in the coordination sphere prevents the determination of the metal oxidation level by the formal rules, "non-innocent," and as the simplest example he mentioned nitric oxide in the composition of mononuclear nitroso complexes. In binuclear nitroso tetracarboxylate complexes, the "non-innocence" of nitric oxide manifested itself especially clear because the inclusion of orbitals of this ligand into molecular orbitals providing the metal–metal bond affects all main characteristics of this bond and all the properties conditioned by them.

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